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13. ABSTRACT (Maximum 200 words)

During the last few years, graphene has emerged as a material of choice in various applications due its unique mechanical and electronic properties. Since 2005, Vorbeck Materials Corporation, presently the only company in the world that is manufacturing graphene in > ton/yr quantities suitable for industrial applications, has been working to advance the application base of graphene. We have recently demonstrated in laser protection applications, that graphene-based suspensions show non-linear reductions in the transmission of high energy laser light. In this study, methods to improve the suspension dispersion and stability were developed. In addition, parameters that yield the unique NLO characteristics of graphene suspensions and the mechanisms leading to the NLO property in graphene suspensions were investigated.

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None

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None

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None

(2) Student/Supported Personnel Metrics for this reporting period.

N/A

(3) Technology Transfer

A suspension of graphene in toluene was sent to the Army's Tank-Automotive Research, Development, and Engineering Center (TARDEC) for evaluation in mock-up laboratory and field experiments. Based on feedback from these evaluations, the product will be refined to optimize performance for a specific Army application.

(4) Scientific Progress and Accomplishments

A well dispersed suspension is necessary for spatial homogeneity and sustainability of the performance of the laser protection materials. If the dispersion quality is poor, aggregates may form and sediment, which will decrease the protection efficiency. Therefore, a critical component for evaluation and use of graphene suspensions for laser protection is dispersion of the graphene sheets into appropriate solvents. Dispersing graphene is challenging because the small distances between the sheets due to the high surface area per weight result in strong van der Waals forces. In this program, the use of improved processing conditions methods, e.g. improved milling and sonication parameters, and the use of surfactants yielded suspensions that remained stable through the evaluation period of several weeks.

Vorbeck prepared a number of graphene suspensions that vary in composition and functionalization and evaluated the linear transmission and non-linear optical performance of the suspensions in collaboration with the Army Research Laboratory (ARL). Our preliminary tests at ARL have shown that Vor-x is a significantly more effective optical limiting material than CNTs and other fullerenes. In fact, some of the preliminary samples ranked as the best optical limiting materials. Vorbeck Materials' Vor-x suspensions showed excellent low-intensity light transmission and a low limiting threshold.

# Graphene in NLO Devices for High Energy Laser Protection

Technical Report

*Contract # W911NF-09-C-0048, CLIN 0001AF*

November 17, 2009

# 1 Introduction

During the last few years, graphene has emerged as a material of choice in various applications due its unique mechanical[1-4] and electronic properties.[1-3,5-14] Most of the ground breaking research has been performed on small quantities of single and multi-stack graphene sheets peeled off from graphite with scotch-tape. For applications where industrial quantities of graphene are needed, however, exfoliation of graphite is a more practical approach. A method for the near-complete exfoliation of graphite to bulk quantities of single sheets of graphene was pioneered at Princeton University and has been licensed to Vorbeck Materials Corporation.[15,16] Vorbeck is presently the only company in the world that is manufacturing single sheet graphene in > ton/yr quantities and has EPA approval for the commercial sale of products based on this material in the US.

Since 2005, Vorbeck has been working to advance the application base of graphene. One of several potential applications for graphene is non-linear optical (NLO) devices for high energy laser protection. NLO devices are critical for protection against laser damage. The proliferation of lasers in military (weaponry/counter measures, range finding, guidance, detection, and designation) and commercial applications has lead to vulnerability of optical systems through inadvertent or intentional damage by exposure to high-intensity laser light.[17,18] This threat extends to ground force and aircrew vision impairment and permanent eye damage. Unintentional damage to sensors and eyes from friendly or commercial laser systems is a significant concern, as well. Similarly, protection against high energy light sources is of concern in various commercial applications.

Sensor (including eye) protection can be achieved by blocking, scattering, diffracting, or absorbing incoming laser light. Current solutions include shutter systems, fixed-line filters, dyes, and/or reflective technologies. Limitations of these systems include slow response time (shutter systems), noticeable color distortion (filters), narrow band protection (filters), low saturation thresholds (Reverse-Saturable Absorbing (RSA) NLO dyes), and insufficient magnitude of the non-linear effect (metal nano-particles, carbon nanotubes and other fullerenes suspensions). A more detailed background of current state-of-the-art materials is provided in Section 1.1.2. To address the limitations of the state-of-the-art, Vorbeck has been evaluating the use of graphene suspensions as protection against high energy lasers. Vorbeck along with the Army Research Laboratory (ARL) have previously observed that graphene-based suspensions show non-linear reductions in the transmission of high energy laser light. In the study reported here, parameters that yield the unique NLO characteristics of graphene suspensions and the mechanisms leading to the NLO property in graphene suspensions were investigated.

## 1.1 Background

### 1.1.1 Vor-x Graphene

Vor-x functionalized graphene sheets used in this work are produced by splitting apart graphite oxide (GO). GO contains epoxy, hydroxyl, and carboxyl side groups attached to the graphitic backbone and has a C:O ratio of ~ 2.[15,19] As illustrated in Figure 1, following the oxidation process, GO is thermally expanded to yield single graphene sheets.[15,19] During the thermal exfoliation, GO is also strongly reduced and the C:O ratio of the resultant graphene increases to ~ 22. Due to the release of $CO_2$ during the reduction stage, the carbon backbone also acquires lattice defects.[15,16,20] Since graphene produced by this approach is different than a perfect graphene sheet, we refer to this form of graphene as functionalized graphene sheets and label it as Vor-$x_n$ where 'n' designates the C:O ratio. The processes of oxidation and exfoliation can be controlled to yield Vor-x with varying amounts of hydroxyl, epoxy, and carboxyl functional groups with carbon to oxygen (C:O) ratio ranging from 2 to 500. In a complementary fabrication method, GO is first split into single graphene oxide sheets by ultrasonication and then reduced chemically.[13,14]

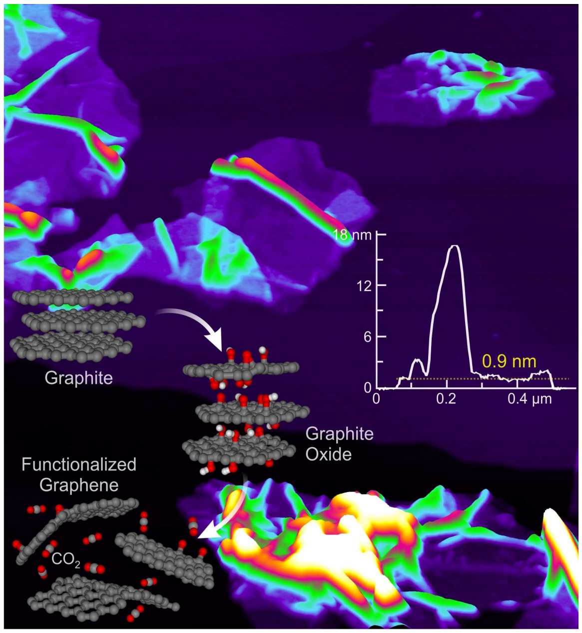


**Figure 1. Atomic Force Microscopy (AFM) images of functionalized graphene sheets on an HOPG substrate. The Vor-x sheets are produced by the exfoliation of graphite oxide (schematic insert) and exhibit folding along lines of functional groups (especially epoxides).**

Collaborators at Princeton University have demonstrated that functional groups or lattice defects can lead to kinks in the Vor-x as shown in the atomic microscopy (AFM) images of Figure 1.[15,16,19] One important type of defect in graphene is the 5–8–5 defect, which has a lower energy on the curved graphitic surfaces and thus can give rise to curvature or crumpling in graphene.[23] This curvature also becomes evident when the equilibrium structures of the sheets containing such defects are determined computationally. Two main advantages of this crumpled graphene structures are: (i) the sheets cannot stack up to the graphitic structure easily; and (ii) they cannot be rolled into nanotube structures due to the stabilizing effect of the wrinkles as support corrugations.

## 1.1.2 Non-linear Optical (NLO) Devices

One of the most important requirements for sensor protection is for the device to be effective over the entire operating wavelength band of the sensor system.[22] For military systems, the optical range can include UV, visible, near IR (night vision), and mid-to-far IR (heat sensing) bands. For protection in the visible band, ambient light transmission should be at least 40%, and transmission in the IR bands should be ~ 85%. Another important requirement is the temporal bandwidth of the protective device. Lasers with 10 ns pulses are considered to be the most common battlefield threat but the optical limiting device should also be able to protect against shorter pulse, long pulse (40 ns to 1 ms) and continuous wave (> 1 ms pulses) threats.

The ultimate test of the protective device is that it prevents sensor ineffectiveness and damage. Each optical system has a maximum permissible exposure (MPE) limit and, for eyes and most military sensor systems, this limit is quite low. It is critical that the protective device have a limiting threshold that is below the MPE of the system it is protecting.

Sensor (including eye) protection can be achieved by blocking, scattering, diffracting, or absorbing incoming laser light. Current solutions include shutter systems, fixed-line filters, dyes, and/or reflective technologies. Shutter systems detect incoming radiation and close the aperture to protect the optical system. The response time of the best shutters (10 ms) is too slow to protect against pulsed laser threats. Filters selectively eliminate two or three distinct wavelengths of incoming light. This leads to noticeable color distortion in the optical system and cannot protect against the increasingly broad range of

wavelengths generated by current laser systems. Reflective technologies are not effective at all incident angles of light and are therefore especially ineffective for curved and complex surfaces.

As passive systems that can protect against a range of wavelengths and allow sufficient light transmission at low intensities, NLO systems are the preferred means of protection. NLO materials allow less transmission of light at higher fluences and this effect has been seen in both absorbing and scattering materials. Reverse-Saturable Absorbing (RSA) dyes, such as carbocyanine, have a low limiting threshold and therefore have strong potential for protecting eyes and sensitive electronics. However, even RSA dyes saturate at intensities generated by many laser systems and lose their non-linear absorbing properties beyond this point. Another problem with many non-linear absorbers is that they do not recover quickly. Once hit with a pulse of laser light they are not effective against subsequent laser pulses for up to several seconds. Non-linear scatters, such as metal nanoparticles, carbon nanotubes and other fullerenes, show broadband protection and are effective at very-high light intensities, however, the magnitude of the non-linear effect is not sufficient and the limiting threshold is too high to protect sensitive military optics.

# 2 Experimental

Isopropyl alcohol, citrus terpene, isoparaffinic hydrocarbons, dibromomethane, and toluene were used as received from chemical suppliers such as Aldrich and Spectrum. Commercial surfactants were used as received from respective distributors. Four grades of functionalized Vor-x prepared by Vorbeck Materials, Vor-$x_{50}$, Vor-$x_{20}$, Vor-$x_{15}$, and Vor-$x_{2}$, were used. As discussed in Section 1.1.1, the functionalization of the Vor-x graphene surfaces consists primarily of hydroxyl and epoxide groups with a smaller number of carboxyl groups also on the surface. Since the functional groups are all oxygen based, the degree of functionalization is reported as the carbon-to-oxygen (C:O) ratio, which provides a measure of how many carbon atoms within the two dimensional graphene sheet are modified with an oxygen containing group. For example, the samples designated Vor-$x_{50}$ have a C:O of 50:1. The C:O ratio was measured by bulk elemental analysis of the Vor-x powder samples.

Suspensions of graphene in the respective solvents were prepared using an attrition mill, high-shear mixer, high power sonication, or a combination thereof. In some formulations, commercially available surfactants were included to aid in suspension stability. The dispersions were characterized for particle size with laser diffraction. Samples were tested for transmission characteristics and non-linear optical properties at the Army Research Laboratory (ARL).

# 3 Results and Discussion

## 3.1 Dispersion and Suspension Stability

A well dispersed suspension is necessary for spatial homogeneity and sustainability of the performance of the laser protection materials. If the dispersion quality is poor, aggregates may form and sediment, which will decrease the protection efficiency. Therefore, a critical component for evaluation and use of graphene suspensions for laser protection is dispersion of the graphene sheets into appropriate solvents. Dispersing graphene is challenging because the small distances between the sheets due to the high surface area per weight result in strong van der Waals forces.

The extent of functionalization affects the dispersion of Vor-x in solvents. Increasing the number of oxygen functional groups on the surface increases the polarity of the sheets. Sheets with more functional groups are easier to disperse in polar solvents and sheets with less functionality disperse more easily in non-polar solvents. This creates a trade-off between the type of solvent used and the type of Vor-x that can be easily stabilized in solution. As initial solvents, we used isopropyl alcohol as a polar solvent that can be used to disperse less functionalized Vor-x to a certain extent and citrus terpenes/isoparaffinic hydrocarbon solvents as the non-polar solvent. Dilute suspensions in e.g. isopropanol and isopropanol+water mixtures were stable for several days. After several days in the lab, the samples showed some agglomeration and sedimentation of particles. The sedimented particles could be quickly redispersed by agitating the samples, but the particles would sediment again, meaning that these suspensions were not sufficiently well dispersed for longer term applications.

Suspension stability was improved in subsequent rounds by improvements in processing conditions, e.g. milling and sonication parameters, plus addition of surfactants. Several commercially available surfactants and mixtures of surfactants were examined at a range of surfactant concentrations (varying surfactant-to-graphene ratios). Using such methods, suspensions could be prepared in a range of solvents including isopropanol, citrus terpenes, toluene, etc. Certain suspension combinations were found to remain stable through the evaluation period of several weeks. Longer term observation is ongoing.

## 3.2 NLO Response

The primary objective of this program was to determine the factors affecting the non-linear optical properties of graphene suspensions. One potential factor is the extent of graphene functionalization as the different levels of functionalization affect multiple properties of the graphene sheets. When a carbon atom in the graphene sheet is functionalized, the bond hybridization changes from planar $sp^2$ to tetrahedral $sp^3$. This change disrupts the planar conjugation and electron de-localization in the graphene sheets and so reduces the conductivity of the sheet. Also, since the functional groups of the graphene surface are not uniformly distributed but tend to cluster into seams in order to relieve lattice strain, the functionalized graphenes consist of a mix of conductive non-functionalized regions and non-conductive, highly-functionalized regions. As the extent of functionalization increases (i.e. the C:O ratio decreases), the size of the conductive domains decreases. The size of the conductive regions, in addition to the over all conductivity of the sheet, is expected to affect how the graphene sheets interact with photons.

Non-linear transmission curves were measured at ARL for suspensions made using Vor-x with different extents of functionalization. Initial results demonstrated that Vor-$x_{15}$ suspensions were more effective than Vor-$x_{50}$ suspensions. One interpretation of this observation is that more highly functionalized graphene is desirable for better optical response. However, when functionalized Vor-$x_2$ suspensions were evaluated, they were less effective than both the Vor-$x_{15}$ and Vor-$x_{50}$ samples. While, functionalization of the graphene surfaces appears to have an effect on the non-linear transmission behavior of the suspensions, the absolute extent of functionalization alone does not completely determine the performance of the material.

Besides graphene functionality, the interaction between the graphene sheets and the suspension solvent can also have a role in the NLO response. To investigate the effect of solvent and solvent mixtures, a set of isopropanol + water solutions were used as solvents for Vor-x functionalized graphene suspensions. In these experiments, Vor-$x_{20}$ (with a C:O of ~ 20:1) was used and the optical limiting performance of the suspensions was evaluated at ARL. As shown in Figure 2 the solvent mixtures with more water have a higher relative transmittance and this effect increases as the water fraction in the solvent increases. Water has a higher surface tension and a higher boiling point than isopropanol, and thus the test results indicated that there is a trend in the relative transmittance of the samples that correlates with solvent surface tension and boiling point.

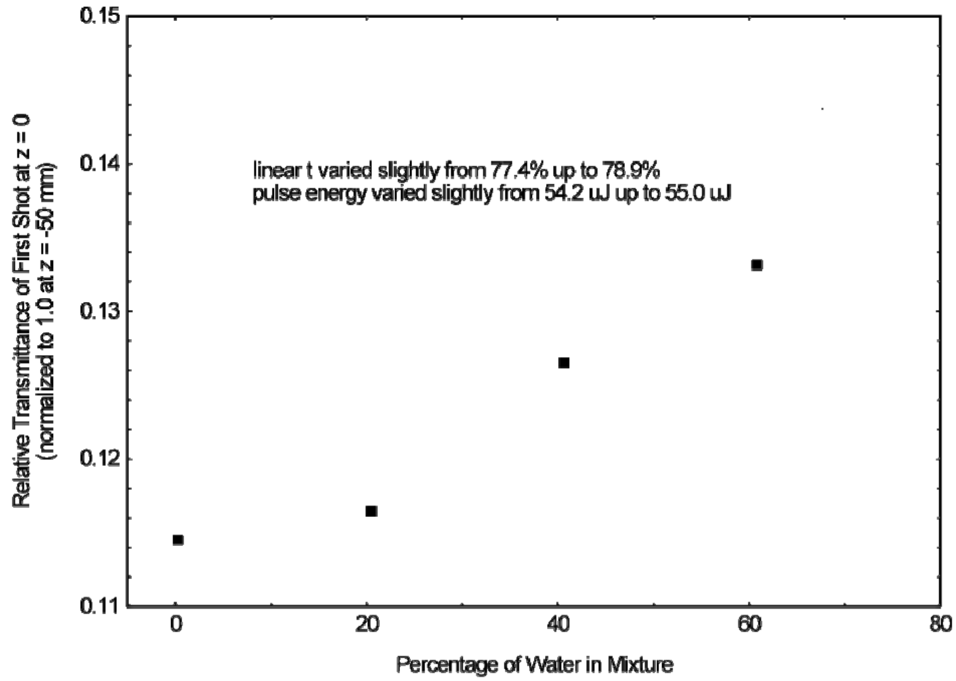


**Figure 2. Effect of varying the ratio of water to isopropyl alcohol in graphene based suspensions. The linear transmittance was 78%.**

Additional experiments at ARL have indicated that non-linear scattering is the primary mechanism by which Vor-x suspensions block intense laser light, as opposed to non-linear absorption. Diffuse light scattered from the Vor-x suspensions can be directly observed perpendicular to the path of the incident light. Scattering is a desirable mechanism for defeating high-energy lasers since non-linear absorbing materials can become completely saturated at high-intensities. While the light maybe directly scattering from the Vor-x particles themselves, the non-linear scattering is believed to be caused by bubble formation in the suspensions. In this mechanism, incident light heats the Vor-x particles and the localized heating of the suspension creates a vapor bubble. The more intense the incident light, the greater the heating effect and the larger the bubble that is created, leading to non-linear scattering. Bubble formation could also be caused by partial vaporization of the Vor-x particles themselves as they are hit by the high energy laser. Similar mechanisms have been proposed for the weaker non-linear transmission effects seen in buckyball and carbon nanotube suspensions.

The bubble mechanism is supported by the observed trend of solvents with varying vapor pressures and heats of vaporization in Figure 2. It is expected that the volatility of the solvent mixtures would impact bubble formation and therefore change the transmission behavior, if bubble formation is the dominant mechanism. As expected, the solvent mixtures with more water (which has a higher surface tension and higher boiling point than isopropanol) have a higher relative transmittance and this effect increases as the water fraction of the solvent increases. However, the effect of the solvent does not significantly alter the performance of the graphene – with a change from 0% to 60% water, the relative transmittance only increases from 11.5% to 13.4%. This indicates that there is solvent flexibility in the graphene suspensions, but also indicates that the interaction between the solvent and the suspended particles does play a role in the nonlinear optical effects in the graphene suspensions, likely through a bubble formation mechanism.

The results discussed above were performed using a “single-shot” experiment. Additional testing in which the samples were exposed to multiple laser pulses (“multi-shot” experiments) gave interesting results as shown in Figure 3. After being exposed to multiple laser pulses, the linear transmission of the suspensions with lower particle concentrations started to rise with each successive “shot”. The relative transmittance of a dilute suspension exposed to 20-30 laser pulses could even go above one, indicating that the suspension allowed a higher percentage of light through at high intensities than at low intensities

- the exact opposite of the non-linear effect seen after one shot. More concentrated suspensions did not show the same effect after multiple shots. A similar phenomena of an increase in transmission with multiple pulses has been reported for multi-walled carbon nanotube based suspensions and was attributed to thermal lensing.[23]

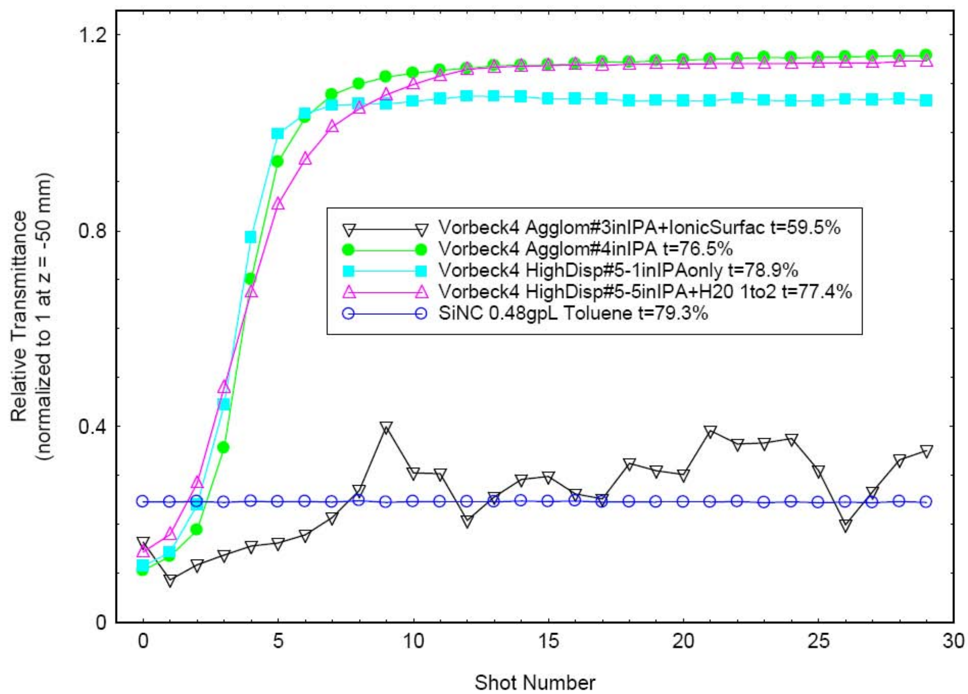


**Figure 3. Transmission behavior of graphene based suspensions with successive laser shots.**

# 4 Conclusions

Vorbeck has preparing a number of graphene suspensions that vary in composition and functionalization. Through a combination of processing and surfactant addition, stable suspensions were generated. The linear transmission and non-linear optical performance of the suspensions were acquired in collaboration with the Army Research Laboratory (ARL). Based on our studies performed to date, we have established a strong proof-of-concept base for application of graphene based suspensions for high energy laser protection.

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